Optical relaxation in organic impurity crystals.

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Summary

In this thesis experimental techniques are described that are extensions of two existing coherent spectroscopic methods (chapter 3). A theoretical framework capable of explaining temperature and coherence exchange effects in molecular mixed crystals is outlined (chapters 2 and 4). Finally the feasibility of near-resonance light scattering and relaxed fluorescence line narrowing methods is examined both theoretically (chapter 5) and experimentally (chapter 6).

In chapter 3 a saturation hole burning technique is presented, based on the idea that the lineshape of the hole, burnt by an intensity-modulated saturating laser beam, may be extracted from the fluorescence generated during the probing process with a second intensity-modulated beam: the relevant fluorescence is the one detected on the sum or difference of both modulation frequencies. This method allows the measurement of non-persistent holes and this is experimentally demonstrated on the vibrationless electronic transition (origin) of pentacene in naphthalene. Further an optical free induction decay technique is described, involving the use of extra-cavity laser frequency switching: this enables the determination of sub-nanosecond dephasing times and is illustrated by an experiment on pentacene in p-terphenyl. The major restriction to the feasibility of both techniques proves to be the enhancement of power saturation by bottleneck effects in the population cycling due to the presence of triplet states of long lifetimes.

Much attention is devoted to a dephasing theory in a form adapted to the terminology of optical spectroscopy. Optical versions of the well-known Redfield and linear response theories are presented in chapter 2 in a detailed fashion. Far less known (at least in the optical literature) is the result discussed here, that coherence exchange phenomena are microscopically interpretable using either formalism: this immediately provides the so far not recognized link between these theories and those recently proposed for optical exchange based on stochastic interactions.

Particularly emphasized is the finding that exchange only occurs among resonant transitions and is described in terms of interfering inelastic processes. Armed with this knowledge, in chapter 4 the situation typical for molecular mixed crystals is discussed. Explicit expressions for the relevant (linear and quadratic) electron-phonon coupling parameters are derived: these are different from those customarily used. Commonly electron-phonon coupling effects are discussed in terms of two-level lineshape theories set up for inorganic systems. In contrast with this the presented discussion is given in terms of Redfield theory applied to both two-level and four-level models for organic impurity systems. Expressions are derived for the dephasing induced by acoustical, optical and (pseudo-) local modes. Within the two-level models (quasi-) exponential activation is induced by pseudo-local and optical phonons, but it is shown that the validity of these theories is only warranted if their bandwidths are sufficiently large. When this condition is not satisfied, the reduction scheme has to be altered: the introduced four-level model including pseudo-local modes proves to explain the experimentally found dephasing characteristics of pentacene in various host crystals. A further outcome of this theory is that coherence exchange in optical transitions is induced by phonon anharmonicity and only occurs when residual dephasing processes play a minor role.

A simple theory of non-Markovian effects in resonance scattering spectra (chapter 5) is used to illustrate why interest revived in these techniques next to the coherent methods. Exchange proves to be an example of such an effect. The ratio of the resonance Raman and fluorescence intensities is shown to directly measure the proper dephasing time only in case of correlated fluctuations in the initial, intermediate and final levels or under conditions of spectral resolution. In contrast to the Rayleigh-fluorescence ratio it is not sensitive to triplet bottleneck effects. Unfortunately the measurements performed on pentacene in naphthalene (chapter 6) demonstrate that the usefulness of these methods is seriously limited generally by interference with

other transitions and by inhomogeneous broadening effects. Experimentally indications are found that the above ratio (and consequently the pure dephasing time) is sensitive to concentration variations in this system.

Strong correlations between the inhomogeneous distributions of the distinct transitions in conjunction with site selective vibrational relaxation found for this system turn out to cause narrowing effects in relaxed fluorescence: from a temperature dependent study vibronic relaxation times are determined. Vibrational relaxation times are extracted from Raman line width measurements: these reveal that pseudo-local modes also play a crucial role in the groundstate vibrational dephasing. The observed behaviour is compared with a model involving vibrational exchange effects: quite unexpectedly intermediate rather than fast vibrational exchange seems to be the most probable dephasing mechanism within the groundstate manifold.